Indian J. Phys. **77B** (6), 673-676 (2003)

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AN INTERNATIONAL JOURNAL

IJP

Dielectric relaxation in para-methyl acetophenone, pyridine and their binary mixtures in benzene solutions

K K Gupta* and P J Singh

Department of Physics, M S. J. College,
Bharatpur-321 001, Rajasthan, India

E-mail kkguptakkg@indiatimes.com

Received 6 May 2003, accepted 6 August 2003

Abstract : The dielectric behaviour of para-methyl acetophenone (PMA), pyridine and their binary mixture as liquid dielectric samples have been studied at microwave frequency 8.93 GHz. in dilute solutions of benzene at temperature 303, 313, 323 and 333K The various dielectric parameters have been evaluated by the observed data for the system and the results have been interpreted on the basis of H- bonding and inductive effect due to the presence of methyl group and compared with the results of acetophenone The thermodynamical parameters indicate that the cooperative orientation of the pure molecules changes into non-cooperative orientation in 1 1 mixture composition Comparative study of free energy of activation for the dielectric relaxation and viscous flow suggests the presence of solute-solvent interactions.

Keywords Dielectric parameters, inductive effect, cooperative and non-cooperative orientation

PACS Nos. . 77.22 Gm, 31 70 Dk

The dielectric studies have been widely utilized by several workers [1-8] to investigate the molecular structure of various systems. The relaxation times and dipole moment gives valuable information about the molecular motions. Study of dielectric behaviour of mixtures of polar molecules under varying conditions of compositions and temperatures has evoked considerable interest. Recently, the authors studied [1] some rigid polar molecules and their mixture and found formation of complexes. Singh and Sharma [8] have studied the binary mixture of PMA and dimethyl sulphoxide in dilute solutions in benzene, at different temperatures and found solute-solute/ solvent interactions.

Khanna and Bhatnagar [9] studied the dielectric relaxation of acetophenone and benzophenone at different temperatures in non-polar solvent, Ganbahadur *et al.* [7] reported the dielectric measurement data for some acetophenone derivatives at microwave frequency 10 GHz. in non-polar solvents, Baliah and Aparajithan [10] reported the dipole moment of PMA in benzene solution at 30°C. In general, there appears to be limited information for PMA concerning the effect of temperature, concentration and its binary mixture with amines in non-polar solvent.

The existing literature shows that elaborate work has been done for pyridine and PMA. But, no work has been reported so far for their binary mixtures. It is hoped that dielectric relaxation studies of the mixture of pyridine and PMA will be helpful in better understanding the dependence of relaxation behaviour on the composition and temperature of the mixtures.

The dielectric constant ϵ_0, ϵ', ϵ_∞ and dielectric loss ϵ'' of pyridine, PMA and their mixtures have been plotted against their weight fraction in benzene at four temperatures 303, 313, 323 and 333K. The slopes of these plots are a_0, a', a_∞ and a'' respectively reported in Table 1. It is clear from Table 1 that the variation of a' and a'' values of individual components and their binary mixture compositions have same trend and order of change with temperature is also the same. This supports our expectations that internal fields of the mixtures are not different from those of pure components in benzene solution.

The values of most probable relaxation time τ_0, the relaxation time $\tau(1)$ and $\tau(2)$ the molecular dipole moment (μ) and the

* Corresponding Author.

Table 1. Values of a_0, a', a'' and a_∞ of single components as well as their mixtures in benzene solutions at different temperatures

Substances	Temp. (K)	a_0			a_∞
Pyridine [1]	303	6 79	6 27	1 66	0 48
	313	6.45	6.04	1.47	0.45
	323	6 11	5.79	1.26	0 44
	333	5 82	5.55	1 13	0 42
Pyridine 75%	303	6.38	5.40	1 98	0.34
+	313	6.09	5.30	1.74	0 29
Paramethyl acetophenone 25%	323	5.80	5.20	1 54	0 26
	333	5 42	4 98	1 35	0 18
Pyridine 50%	303	6.45	5.21	2 17	0.54
+	313	6.04	5 08	1 90	0 42
Para methyl acetophenone 50%	323	5.63	4.95	1 63	0.37
	333	5 29	4.82	1 36	0.29
Pyridine 25%	303	7 28	5.16	2.90	0.37
+	313	6 67	4 97	2.56	0.35
Para methyl Acetophenone 75%	323	6 21	4 87	2.24	0 32
	333	5 78	4.76	1 94	0 27
Para methyl Acetophenone	303	7 90	5 13	3 61	0 16
	313	7 31	5.03	3 25	0 16
	323	6 78	4.95	2 89	0.16
	333	6 21	4.75	2.53	0 15

Table 2. Values of relaxation times [$\tau(1)$, $\tau(2)$ and τ_0]/ps, distribution parameter (α), dipole moment μD of Pyridine + PMA mixture in dilute solutions of benzene at different temperatures.

Substances	Temp. (K)	$\tau(1)$	$\tau(2)$	τ_0		
Pyridine [1]	303	5.1	5.5	5.0	2.24	0.01
	313	4.7	5.1	4.6	2 24	0.01
	323	4 2	4.6	4.2	2.24	0.01
	333	3.9	4 2	3 9	2.24	0 01
Pyridine 75%	303	7 0	8.8	6 9	2 75	0 06
+	313	6 2	8 1	6 0	2 77	0 06
Paramethyl acetophenone 25%	323	5.6	6.9	5 4	2.78	0 05
	333	5.0	5 8	4 9	2.78	0 03
Pyridine 50%	303	8 3	10.2	8 3	2.72	0 06
+	313	7.3	9 0	7.2	2 73	0 05
Para methyl acetophenone 50%	323	6.3	7 4	6.2	2.71	0.04
	333	5.4	6.2	5 2	2.71	0.03
Pyridine 25%	303	10 8	13 0	11.1	2.94	0 06
+	313	9 9	11 8	10 1	2.89	0 05
Para methyl Acetophenone 75%	323	8.8	10 7	8 8	2 87	0 05
	333	7 7	9.4	7 7	2.85	0 05
Para methyl Acetophenone	303	12 9	13 7	13 1	3 12	0 02
	313	11.9	12 5	12 0	3.08	0 02
	323	10.8	11.3	10 8	3 04	0 01
	333	9 8	10 3	9 8	2 99	0.01

distribution parameter (α) are reported in Table 2. τ_0, $\tau(1)$ and $\tau(2)$ values of PMA are almost same at each temperature. This shows that a single relaxation process exists in PMA molecule. Similar results were obtained for pyridine molecule [1], which shows that no intra-molecular relaxation process exists in pyridine and PMA molecule, because the presence of this relaxation process might have caused significant difference between $\tau(1)$ and $\tau(2)$ values. The values of relaxation times reported by Singh and Sharma [8] for PMA at temperatures 30, 40, 50 and 60°C are 13.0, 11.5, 10.8 and 9.8 respectively, obtained by the method of Gopala Krishna [11], which are comparable with the observed values of the authors.

It is also clear from the table that there is a significant difference between $\tau(1)$ and $\tau(2)$ values of pyridine + PMA mixtures, which shows that intra molecular relaxation process exists in addition to the overall molecular relaxation process. The values of α for the three mixtures composition are slightly higher than the values for the individual components, suggesting that there may be more than one relaxation process in pyridine + PMA mixtures. The value of relaxation time of mixture increases with the increase of concentration of PMA in the mixture, this may be due to the fact that relaxation time of PMA is higher than the relaxation time of pyridine. A plot of relaxation time (τ_0) of mixtures against the concentration of PMA in mixture at different temperatures are shown in Figure 1. The slope of the curve is slightly deviated from linearity near equal mole fraction which may be due to the interaction between the two constituent molecules.

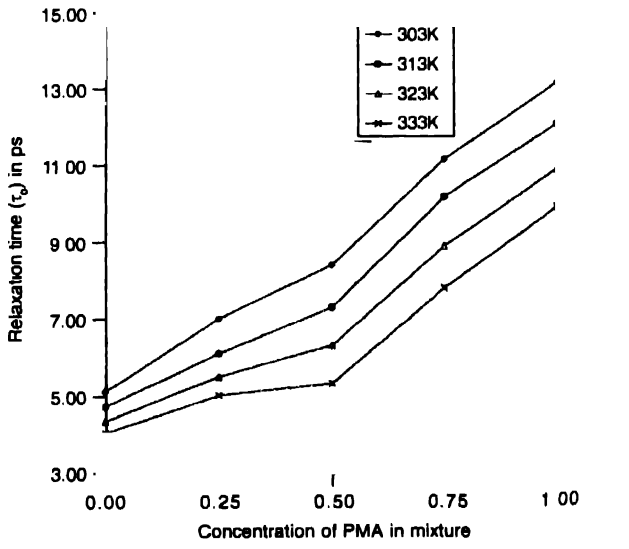

Figure 1. Variation of relaxation time as a function of concentration of PMA in mixtures.

The values of dipole moment (μ) of pyridine, PMA and their mixtures in benzene at different temperatures have been calculated using the method by Koga *et al* [12], which are given in Table 2. It shows that μ values of the mixture lie between the μ values of its constituents, at each temperature. The μ values of PMA are comparable well with the observed values obtained by Singh and Sharma [8] at temperatures 30, 40, 50 and 60°C are 3.06, 3.07, 3.08 and 3.08 respectively, by Gopala Krishna's method [11] and 3.19 by Baliah and Aparajithan [10] at 30°C.

Figure 2 shows the plot of tan δ *vs.* concentration of PMA in the mixture at different temperatures. It is seen form the figure that the absorption in the mixture is greater than that in pure liquids, maxima in the tan δ curve occurring at 0.50 concentration of PMA in the mixture. It may be explained by using the Debye's equation [13] for tan δ for a dilute solution of a polar liquid in a non-polar solvent :

$$\tan\delta = \frac{(\epsilon'+2)^2}{27KT}\cdot\frac{4\pi\times N\mu^2}{}\cdot\frac{\omega\tau}{\left(1+\omega^2\tau^2\right)}.$$

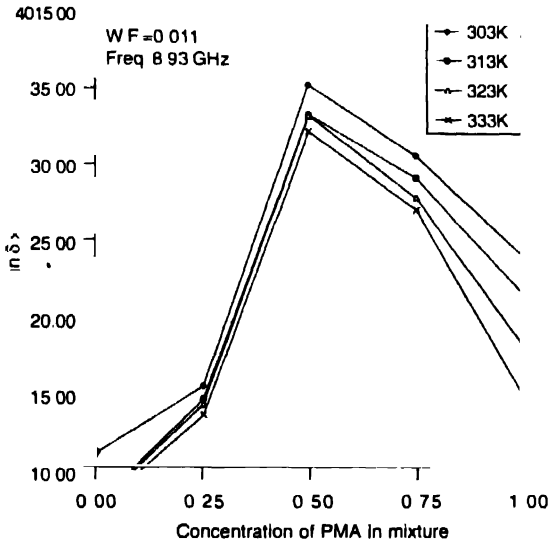

Figure 2. Variation of tan δ in benzene as a function of concentration of PMA in mixtures.

This equation suggests that the absorption will increase, if the dipole moment μ and relaxation time τ increase. Applying Debye's equation to our case, the formation of the complex will increase the dielectric absorption due to the following consideration. In the complex, the dipole moment can be taken as $(\mu_1+\mu_2)$, μ_1 and μ_2 being the dipole moments of the constituent molecules. For n molecules of each liquid forming the complex, the absorption would be proportional to $n\left(\mu_1^2+\mu_2^2\right)$ for pure liquids, assuming no interaction. On the other hand in the mixture, the absorption would be proportional to the greater term $n(\mu_1+\mu_2)^2$. Regarding the role of τ, it is reasonable to assume that at microwave frequencies, $\omega\tau < 1$ and therefore the term $\omega\tau/(1+\omega^2\tau^2)$ will not affect the tan δ values to a great extent.

The relaxation time values of PMA are higher as compared to acetophenone [1] values obtained by the authors earlier at temperatures 30, 40, 50 and 60°C, they are 7.8, 7.2, 6.7 and 6.0 respectively. This may be due to the fact that inductive effect of methyl group on PMA is positive, so it increases the electron density on aromatic ring. The increase in τ values may also be explained, as there may be a smaller energy barrier to rotation in acetophenone. Placing methyl group in the p- position may then increase the energy barrier to rotation of acetyl group, giving rise to a larger τ for the PMA molecule.

The various thermodynamical parameters *i.e.* the molar free energy of activation (ΔF_ϵ), the molar enthalpy of activation (ΔH_ϵ) and the molar entropy of activation (ΔS_ϵ) for the dielectric relaxation process can be obtained by using the rate process equation [14]. These thermodynamical parameters are given in Table 3. In the case of mixture, the ΔF_ϵ values increase with temperature in a fashion similar to that in case of pure component. This means that the mixture behaves like a single system. Therefore, with the rise of temperature, which results in the fall of the viscosity of the surrounding medium and rise in the thermal energy, the molecules of the system as a whole, require more energy to come to the activated state. It is evident from Table 3 that the molar free energy of activation for viscous flow ΔF_η is greater than ΔF_ϵ. This is in agreement with the fact that the process of viscous flow involves greater interference by neighbours than does dielectric relaxation, as the latter takes place by rotation only whereas the viscous flow involves both the rotational translational forms of motion. The ratio of the energies $\Delta F_\epsilon / \Delta F_\eta$ is less than one, which suggests that the moving units participating in the two processes are identical and that the activation takes place in same degree of freedom because the same bonds have to be broken before either motion is possible. Similar results were obtained by other workers [15, 16].

The values of ΔS_ϵ for relaxation process present an interesting case. The ΔS_ϵ values for the pure component and their mixtures are negative except 1:1 composition of the mixture. The negative value of ΔS_ϵ suggests that the existence of cooperative orientation in the single component system and their mixtures but become non-cooperative in 1:1 composition, resulting into an activated state, which is more disordered than the normal state. It is also clear from Table 3 that the ΔS_ϵ values are highest for the mixture composition having nearly equal moles of the two components. This again indicates that for this particular concentration ratio of the mixture, the interaction between the molecules of two components and their interaction with solvent are enhanced. This also indicates that presence of PMA molecule with pyridine molecules in benzene resulting in the reduction of steric force [17] and the presence of H-bonding.

Table 3. Thermodynamical parameters of single components as well as their mixtures in benzene solutions at different temperatures.

Substances	Temp. (K)	τ_0 (ps)	ΔF_ϵ K cal/ mole	ΔH_ϵ Kcal/ mole	ΔS_ϵ cal/mole/ deg	ΔF_η Kcal/ mole	$x = \Delta F_\epsilon / \Delta F_\eta$
Pyridine [1]	303	5 0	2 08	1.14	−3 10	2.91	0.71
	313	4 6	2 12		−3 11	2 93	0.72
	323	4.2	2 14		−3.07	2.95	0.73
	333	3 9	2 18		−3 11	2 98	0.73
Pyridine 75%	303	6.9	2 27	1.62	−2.12	2 91	0 78
+	313	6 0	2 28		−2 10	2 93	0.78
Paramethyl acetophenone 25%	323	5 4	2.30		−2.10	2 95	0.78
	333	4 9	2 33		−2.12	2 98	0 78
Pyridine 50%	303	8.3	2 38	2 42	0.11	2 91	0 82
+	313	7 2	2 39		0 08	2 93	0 82
Para methyl acetophenone 50%	323	6.2	2 40		0.06	2 95	0 81
	333	5 2	2 38		0 12	2.98	0 80
Pyridine 25%	303	11 1	2 56	1 87	−2 26	2.91	0.88
+	313	10.1	2 60		−2 32	2 93	0 89
Para methyl Acetophenone 75%	323	8.8	2 62		−2 31	2 95	0 89
	333	7.7	2 63		−2.26	2.98	0 88
Para methyl Acetophenone	303	13 1	2.66	1 31	−4 43	2 91	0.91
	313	12 0	2.71		−4.46	2 93	0 92
	323	10.8	2 75		−4.44	2 95	0 93
	333	9 8	2 79		−4.44	2.98	0 93

Acknowledgments

The authors are thankful to the Head of the department of Physics & Principal, M.S.J. College, Bharatpur for providing laboratory facilities. One of them (K. K. Gupta) is indebted to the University Grants Commission for providing MRP to him.

References

[1] K K Gupta, A K Bansal, P J Singh and K S Sharma *Indian J. Pure Appl. Phys* **41** 57 (2003)

[2] A K Bansal, K K Gupta, P J Singh and K S Sharma *J Mol. Liquids* **102/1-3** 173 (2003)

[3] A K Bansal, K K Gupta, P J Singh and K S Sharma *Indian J. Phys.* **76B** 283 (2002)

[4] K K Gupta and P J Singh *Indian J. Phys* **77B** 335 (2003)

[5] A D Vyas and V A Rana *Indian J Pure Appl. Phys* **39** 316 (2001)

[6] A C Kumbharkhane, S M Puranik, C G Akode and S C Mehrotra *Indian J. Phys* **74A** 471 (2000)

[7] R Y Ganbahadur, A C Kumbharkhane and S C Mehrotra *Indian J. Phys* **68B** 363 (1994)

[8] P J Singh and K S Sharma *Indian J Pure Appl Phys* **34** 1 (1996)

[9] R K Khanna and A Bhatnagar *J Mol Liquids* **38** 63 (1988)

[10] V Baliah and K Aparajithan *Tetrahedron* **19** 2177 (1963)

[11] K V Gopala Krishna *Trans Farad. Soc* **53** 767 (1957)

[12] Y Koga, H Takahasni and K Higasi *Bull Chem Soc Jpn* **46** 3359 (1973)

[13] C P Smyth *Dielectric Behaviour and Structure* (New York McGraw-Hill) (1955)

[14] S Glosstone, K J Laidler and H Eyring *The Theory of Rate Processes* (New York McGraw-Hill) Ch 9 (1941)

[15] J M Gandhi and Gopal Lal *J. Mol Liquids* **38** 23 (1988)

[16] C Aggarwal, R Arya, J M Gandhi and M L Sisodia *J. Mol Liquids* **44** 161 (1990)

[17] S M Khameshara and M L Sisodia *Adv Mol. Relax Int Processes* **16** 195 (1980)